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(54) RESILIENT COMPOSITE USEFUL AS SURFACING FOR  
 ATHLETICS

(71) We, MINNESOTA MINING  
 AND MANUFACTURING COMPANY, a  
 corporation organised and existing under the  
 Laws of the State of Delaware, United States  
 of America, of 3M Center, Saint Paul, Minne-  
 5 sota 55101, United States of America, do  
 hereby declare that the invention for which  
 we pray that a Patent may be granted us,  
 and the method by which it is to be per-  
 10 formed, to be particularly described in and  
 by the following statement:—

This invention relates to a composite  
 material comprising bonded particulate vul-  
 canised rubber useful as a surfacing or pav-  
 15 ing for athletic activities. In another aspect,  
 it relates to the method for preparing such a  
 composite material.

Briefly, according to the invention, an  
 elastomeric, water permeable composite com-  
 20 prises sulphur-vulcanised rubber particles, par-  
 tially or wholly coated and bonded with a  
 cross-linked, non-cellular, binder having a  
 plurality of isocyanurate and urethane link-  
 25 ages and derived from an essentially solvent-  
 free, polyisocyanate-polyoxyalkylene polyol  
 reaction mixture having low volatility and an  
 NCO/OH equivalent ratio greater than unity.  
 Such composites are useful, for example, in  
 surfacings or pavings for athletic activities.

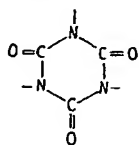
The reaction mixture from which a compo-  
 site according to the invention is formed is  
 curable at room temperature. The term "sol-  
 vent-free" is used in the conventional sense  
 30 to mean essentially free of non-reactive sol-  
 vents and of low volatility.

In preferred embodiments of the invention  
 the rubber particles comprise 50 to 95% by  
 weight, the binder comprises 5 to 50% by  
 weight and the void volume of the composite  
 is in the range 15 to 75%. Such composites  
 40 can be made by at least partially coating sul-  
 phur vulcanised rubber (such as scrap from  
 the treads and/or carcass of pneumatic auto-  
 mobile or truck tyres) with a reaction mix-  
 45 ture of a cross-linked, non-cellular binder  
 having a plurality of isocyanurate and urethane  
 linkages and being derived from an essentially  
 solvent-free, room temperature-curable, poly-  
 isocyanate-polyoxyalkylene polyol reaction  
 50 mixture having low volatility and an NCO/  
 OH equivalent ratio greater than unity; and a  
 trimerising catalyst, and curing the binder  
 to bind the particles in a coherent mass.

Composites made in accordance with the  
 invention are resilient, flexible, elastomeric,  
 55 compressible and have hydrolytic stability,  
 structural integrity, and other physical prop-  
 erties which enhance their eminent useful-  
 ness as a surfacing or paving for athletic  
 60 activities, such as track and field events, tennis,  
 football, and the like. The surfacing can be  
 used for gymnasiums and field houses and for  
 pedestrian or vehicular traffic.

The binder used to bond the vulcanized  
 rubber particles to form the composite of this  
 invention is a crosslinked polyisocyanurate  
 polymer. This type of polymer is broadly  
 65 known in the art and it is characterised by  
 containing a plurality of isocyanurate link-

ages which impart thermal stability to the polymer, such linkages having the formula



These polyisocyanurates can have crosslink densities of 1 crosslink per 400 to 20,000 atomic weight units of polymer, the preferred rubbery polyisocyanurates having a crosslink density of 1 crosslink per 1000 to 5000 atomic weight units. In addition to the aforementioned thermal stability, these polymers, more importantly, are hydrolytically stable and no significant change in physical properties, such as hardness, occurs in these polymers on standing or in use as a binder for the composite, even upon immersion in water or upon being subjected to high humidity and temperature environments (e.g. when tested by the procedure described in "Insulation", August 1968, p. 39). Thus, the desired structural integrity, appearance and physical properties of the composite of this invention are maintained on standing or in use, e.g., even under relatively high humidity and temperature conditions such as 70 to 100% R.H. and about 5 to 70°C.

The polyisocyanurate binder is prepared, in the presence of the vulcanized rubber particles, by trimerizing polyisocyanates, using for this purpose a trimerizing catalyst. As a class, the polyisocyanates are well-known, and the aromatic polyisocyanates and isocyanate prepolymers are preferred in making the binders in the composite of this invention. Representative polyisocyanate compounds which can be used in this invention include such compounds as 2,4- and 2,6-tolylene diisocyanates; 1,5 - naphthylene diisocyanate; 4,4' - diisocyanatophenylmethane; 3,3' - dimethyl - 4,4' - biphenylene diisocyanate; 3,3' - dimethoxy - 4,4' - biphenylene diisocyanate; 3,3' - diphenyl - 4,4' - biphenylene diisocyanate; 4,4' - biphenylene diisocyanate; 3,3 - dichloro - 4,4' - biphenylene diisocyanate; and 4,4',4'' - triisocyanato - triphenylmethane. The so-called polymeric polyisocyanates can be used, such as those obtained by phosphorylation of polyamines prepared by condensing formaldehyde with aromatic amines; particularly useful polymeric polyisocyanates are the polymethylene polyphenyl isocyanates, such as those sold commercially as "Mondur MR" and "MRS", Isonate 901 and 309P, and "PAPI". A list of useful commercially available polyisocyanates is found in "Encyclopedia of Chemical Technology, "Othmer, Second Ed., p. 146-147, Interscience Pub., 1967 and in Appendix A of "Polyurethanes: Chemistry and Technology, by Saunders & Grisch, Part I, Interscience Pub. (New York,

1962). Urethane prepolymers, can be used and are known (e.g. see U.S. Patent Specifications Nos. 3,073,802 and 3,054,755), such prepolymers being prepared by reacting an aromatic or so-called polymeric polyisocyanate with a polyol such as polyoxyalkylene polyol, typically, polypropylene glycol, using an excess of polyisocyanate. Mixtures of various polyisocyanates can be used to prepare the binders in the composite of this invention. The polyisocyanates which are preferred are those commonly used in conjunction with polyols to prepare polyurethanes, including so-called urethane prepolymers.

The binder used in this invention is prepared by reacting greater than stoichiometric amounts of polyisocyanate with polyol; conventional polyols used in making polyurethanes can be used. Broadly, the polyols can have molecular weights between 250 and 3,000 or even as high as 5000. Where a harder binder is desired, the polyol will generally have a hydroxyl equivalent weight of 130 to 400 (i.e. one reactive hydroxyl group per 130 to 400 molecular weight of polyol). Where a softer, more rubbery binder is desired, the polyol will generally have an equivalent weight of 400 to 1000. The polyalkylene ether polyols are polyols generally made as condensates of ethylene, propylene, or butylene oxides with pentaerythritol, sorbitol, sucrose, methylglucosides, or low molecular weight polyols, such as propylene glycol, tri-, tetra-, penta-, hexa- methylene glycols, 1,3-butylene glycol, 1,3-(2-ethyl)hexane diol, 2,2,4-trimethyl - 1,3 - pentane - diol, trimethylol propane, 1,2,6-hexane triol, or phenyl-diisopropanolamine. Polypropylene ether polyols are particularly useful and readily commercially available (see Appendix B of Saunders & Frisch, supra).

The binder in the composites of this invention is made from polyisocyanate-polyol reaction mixtures, the mixtures used having NCO/OH equivalent ratios greater than 1. The rate is preferably at least about 1.2/1, and can be as high as 12/1 or greater. Typically, the NCO/OH ratio will be 1.2/1 to 6/1. Generally, the greater this ratio, the greater amount of isocyanurate linkage in the resulting product and the greater its hardness. The preferred products are those which are highly crosslinked by reason of having about 20 to 85% of the isocyanate groups in the reaction mixture converted to isocyanurate linkages, the rest of the isocyanate-derived linkages comprising urethane linkages or, in the event that moisture is present during polymerization, urea linkages.

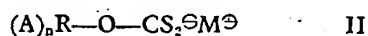
The catalysts used for catalyzing the polymerization of the aforementioned mixtures of polyisocyanates and polyols will generally be basic catalysts which promote the formation of isocyanurate rings and the formation of urethane linkages. Preferred catalysts are xan-

thate salts which can be represented by the general formula:



in which  $\text{M}^{\oplus}$  is a cation of an alkali metal cation, e.g. lithium, sodium or potassium, or a quaternary ammonium cation, e.g. tetraalkyl ammonium, R is an alkyl, which can be substituted with ether oxygen atoms and/or hydroxyl substituents, e.g. alkoxyalkyl, alkoxy-alkoxyalkyl, hydroxyalkyl, and (hydroxy-alkoxy)alkyl, R preferably having 2 to 18 carbon atoms, O is oxygen, and S is sulfur. Representative catalysts of this type include tetra-methyl-ammonium ethyl xanthate, potassium isobutyl xanthate, sodium n-hexyl xanthate, potassium 2-methoxypropyl xanthate, sodium 1 - methoxy - 2 - propyl xanthate and sodium 6 - methyl - 4,7 - dioxo - 2 - octyl xanthate.

A useful novel subclass of xanthate salt catalysts are those of the formula:



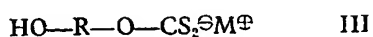
where A is a hydroxyl group or a hydrogen atom, R is a polyvalent saturated straight or branched aliphatic group (which can have one or more catenary ether oxygen atoms) such as alkylene, alkyleneoxyalkylene, or poly-(alkyleneoxyalkylene), said alkylene moieties being straight or branched chain and having, for example, 2—18 carbon atoms, with the proviso that when A is a hydrogen atom, R has one or more of said catenary ether oxygens (e.g., R is alkyleneoxyalkylene), n is an integer equal to x—1, where x is the valence of said polyvalent saturated aliphatic group, n preferably being 1 to 3, and  $\text{M}^{\oplus}$  is a cation of an alkali metal cation, e.g., sodium, potassium, or lithium, or a quaternary ammonium cation, e.g. tetra-alkyl-ammonium (the alkyl groups of which can have, for example, 1 to 18 carbon atoms each).

The xanthate salts of Formula II, and polyol solutions thereof, used in this invention are relatively storage stable. The polyisocyanate or polyisocyanate-polyol mixtures mixed with such salts or solutions thereof are reaction mixtures having a desirable pot-life at ambient temperatures, e.g., 0 to 38°C. As such, the reaction mixtures are latently curable and can be readily applied, e.g. as a coating, or shaped and the applied or shaped reaction mixture then allowed to cure slowly or moderately heated, e.g. to 102°C., to effect rapid cure. The gel times of such reaction mixtures are relatively independent of the bulk of the applied or shaped reaction mixture and high catalyst levels can be used to get a "tight" or complete cure. Further, the gel times are not strongly dependent on catalyst concentra-

tion and the latter do not have to be accurately measured. Xanthate catalysts useful in the present invention are described in U.S. Patent Specification No. 3,711,444.

A particularly useful procedure for making the xanthate salts of Formula II comprises, as a first step, reacting a precursor polyol, such as dipropylene glycol, with a source of strong base such as alkali metal, or hydroxide or alcoholate thereof, e.g. sodium, sodium hydroxide, or sodium methoxide, to prepare the corresponding monosalt of said polyol. Said mono-salt is then reacted, in a second step, with an amount of carbon disulfide equivalent to the amount of base, or in excess thereof to prepare the xanthate salt having the above-described formula. Preferably, in the first step, the source of base is reacted with a stoichiometric excess of the polyol so as to produce a polyol solution of the mono-salt, and this solution then, in the second step, is reacted with the carbon disulfide, so as to obtain the xanthate salt in the form of a solution thereof in said polyol. The solutions can have low concentrations, e.g. as low as 0.01 molal, though concentrations of greater than 0.03 molal are preferred when polyisocyanates having significant inherent acidity are used in this invention. Use of the xanthate salt catalyst in the form of such a solution enables one to admix intimately and rapidly the catalyst with the polyisocyanate, as well as with any polyol that may be present in admixture therewith. The polyol solvent in such solutions is, of course, a reactive solvent for the polyisocyanate as well and reacts therewith to form urethane linkages. It should be understood, however, that use of the xanthate salt in the form of a polyol solution is not essential to the practice of the broader aspects of this invention, though such solutions are preferred for reasons given above. Where the xanthate salt has catenary ether oxygens in its structure, such a salt will be miscible or readily compatible with the reactants where the polyisocyanate reactant used is a prepolymer based on a polyalkyleneoxy polyol, such as polypropylene ether glycol, or where the polyisocyanate is polytrimerized in the presence of such a polyol. Preferably, said xanthate salt has one or more hydroxyl groups in its structure such that, in addition to promoting the trimerization of the isocyanate groups, it reacts therewith forming urethane linkages and thus the catalyst reacts therewith forming urethane linkages and thus the catalyst becomes an integral part of the resulting polymer and will not exude therefrom. By becoming an integral part of the polymer, applied or shaped articles of the latter will not exhibit any significant shrinkage or weight loss, even when heated under vacuum.

The xanthate salts preferred in the practice of this invention are those having the general formula



III

where R is alkyleneoxyalkylene or poly-  
(alkyleneoxy) alkylene, such as propylene-  
oxypropylene and poly(propyleneoxy) propylene, and where M is an alkali metal cation  
such as sodium, said xanthate salt preferably  
having a molecular weight from 200 to as  
high as 2,000 to 3,000 or higher. Representa-  
tive xanthate salts which can be used include  
sodium dipropylene glycol monoxanthate,  
sodium tripropylene glycol mono-xanthate,  
sodium diethylene glycol mono-xanthate,  
sodium triethylene glycol monoxanthate,  
sodium polypropylene glycol monoxanthate,  
sodium 1,2,6-hexane triol monoxanthate,  
sodium poly(oxypropylene) triol monoxanthate,  
and the corresponding potassium xanthate  
salts.

The amount of catalyst used in trimerizing or polymerizing the polyol-polyisocyanate reaction mixtures used in this invention will vary, depending on the particular catalyst and reactants used. Generally, the amount of catalyst to be used will be less than 10 wt. % of the polyisocyanate reactant, and usually from 0.5 to 5 wt. % of the polyisocyanate. Functionally stated, the amount of catalyst to be used will be that amount sufficient to catalyze the trimerization polymerization of the reaction mixture at the desired temperature.

Where a more highly crosslinked polymer is desired, the polyol-diisocyanate reaction mixture can include a conventional triisocyanate or a triol. The reaction mixture can also include modifying monoisocyanate or alcohols such as 1,4-butane diol, butyl Cellosolve, butyl Carbitol, and oleyl alcohol, to impart special properties to the polymer product, such as the degree of final hardness.

The particulate vulcanized rubber can be obtained by shredding, chopping, grinding or otherwise comminuting any vulcanized natural or synthetic rubber, such as vulcanized copolymers of butadiene and styrene (known in the art as SBR rubber), 2-chloro-1,3-butadiene polymers (known in the art as neoprenes), polyisoprene, polybutadiene and copolymers of ethylene and propylene, including blends of such rubbers. Especially useful and economical sources of the rubber particles will be scrap obtained from the treads and/or carcass of automobile or truck tires, and, as such, the vulcanized rubber will contain the conventional rubber compounding chemicals, such as carbon black, sulfur, etc. The sizes of the particles can vary and they can be relatively smooth-surfaced or angular. Preferably, the bulk of the particles will be shreds, cigar-shaped rods, or slivers, particles of such shape aiding in distributing forces applied to the composite during use. Typically, the particles will have sizes such that substantially all pass through a screen with

1.3 to 0.6 cm. openings and are retained on a U.S. Sieve No. 30 or No. 40 screen. Generally, the larger the particles, the greater the permeability of the composite, other things, such as pressure applied during fabrication of the composite and amount of binder, remaining the same.

The relative amounts of particulate vulcanized rubber and binder in the composites can vary, but generally the particulate rubber will amount to 50 to 95 weight percent and the binder will amount to 5 to 50 weight percent, based on the total weight of the composite. In any event, the amount of binder used will be that sufficient to partially or wholly coat the particles such that upon curing the coating, the composite will have structural integrity and can be readily handled. Where it is desirable to prevent degradation of the rubber particles (e.g. due to exposure to air) or where it is desirable to color the composite with pigments, sufficient binder will be used to wholly coat the particles. Of course, the larger the relative amount of rubber particles used in making the composite, the lower will be the raw material cost, the rubber particles being a far less expensive material than the binder. The binder and rubber particles are compatible, and the binder can tolerate large amounts of the latter, and the presence of the particles during the cure of the binder does not adversely affect the manner of cure or the nature of the cured product.

If desired, the composite material of this invention can be colored for decorative, aesthetic, or utilitarian purposes by incorporating into the binder various pigments or colorants. Use of a pigmented binder results in a colored composite in which the vulcanized rubber particles are partially or preferably wholly colored on their surfaces. Also, if desired, the binder can have fillers incorporated therein, such as clay, hollow microspheres, expanded perlite or vermiculite, asbestos, or other fibrous fillers, to modify, increase or change the physical properties of the composite.

Another advantage of the liquid reaction mixture or coating used to form the binder in the composite of this invention is that it is essentially solvent free and of low volatility, that is, it does not contain any significant amount of materials which volatilize during cure of the coating or during use of the composite article. Of course, since the coating is essentially solvent free, there will not be any significant swelling of the rubber particles, nor will the constituents of the coating cause such swelling. During curing, or thereafter, the shaped mass of composite does not perceptibly shrink or expand, and shaped composites with close dimensional tolerances can be made.

Though the composite article of this invention can be made in a form which is substantially impervious or non-porous, for example, to air, water or moisture, it will preferably be made in a porous or permeable form for some applications, such as surfacing for athletics. Such permeable articles can be made by using vulcanized rubber particles which are irregular in shape and variable in size and/or by using an amount of binder such that the particles are coated, either partially or wholly, with sufficient void space or interstitial space left between the coated particles. This void space can amount, for example, from 15 to 75 volume percent of the composite. Such void space will be advantageous where, in the use of the composite as a surfacing, it is flooded with water, for example rainwater, the permeable nature of the composite permitting drainage of such water. Such drainage will also minimize or prevent pressure points, due to sub-surface conditions, from developing between the layer of composite and any surfacing laminated thereon. Such void space also imparts a cushion-like nature and sound absorption to the composite.

In fabricating the composite in a form useful for surfacing, the coated particulate vulcanized rubber can be poured into any suitable mold and allowed to cure, after which the cured composite can be removed from the mold, the molded article having the shape and size of the mold cavity. The composite article can vary in density, e.g. from 0.5 to 1 gram/cc, or greater, the particular density desired being obtained by applying pressure to the mass of coated particles in the mold during its cure, the greater the pressure, the greater the density of the composite article. Curing can take place at various temperatures, e.g. from about 0 to 38°C., and typically room temperature though elevated temperatures, e.g. as high as 204°C. can be used in order to hasten the cure. If desired, hot air can be forced through the permeable mass of coated particles, to hasten cure. Instead of using a mold, the mass of coated particles can be continuously poured onto a desired substrate, such as a moving belt or the like, preferably troweling, tamping, or otherwise shaping it, and allowing it to cure at ambient temperature. The mass of coated particles also can be poured on a desired substrate, such as asphalt, concrete, and the like, troweled, and cured *in situ*. In making prefabricated composite articles useful for surfacing, the mass of coated particles can be cured in bulk and the cured bulk article then cut, sliced, skived, or otherwise divided into smaller articles of desired shape such as boards, tiles or strips with interlocking edges or the like if desired.

In the accompanying drawing, Figure 1, is a perspective view, in partial section, illustrating a layer of composite material of this invention on a suitable substrate; and Figures

2, 3, 4 and 5 are views similar to that of Figure 1 illustrating other embodiments of this invention with the composite material overlaid with other materials to provide laminated surfacings for various purposes. In these figures, like parts are designated with like reference numbers.

Where the composite material of this invention is used as a surfacing, for example, for athletic activities, preformed shapes, such as boards or strips of the composite can be laid on a suitable substrate such as asphalt or concrete and preferably bonded thereto with a layer of a suitable adhesive such as a conventional two-part catalyst-cured polyurethane for a permanent installation or a pressure-sensitive adhesive for a temporary installation. This utility for the composite of this invention is illustrated in Figure 1 of the accompanying drawing where a layer 1 of the composite is shown laid over a substrate 2 such as asphalt and bonded thereto with a layer 3 of a suitable adhesive. In that embodiment, the top surface of the composite is exposed and though this type of surfacing will be useful for many applications, such as a playground, it is within the scope of this invention to apply one or more different layers of polymeric material on top of the composite for special purposes to form a laminated structure. For example, as shown in Figure 2, the top surface of the layer 1 of the composite is covered with a layer 4 of conventional polyurethane which can be formed *in situ* or bonded thereto with a layer 6 of suitable adhesive. The top layer 4 can have rubbery aggregate, such as polyurethane aggregate, distributed over it in a random manner, or embedded therein to provide a relatively rough surface with greater traction on the exposed surface of the assembly. This embodiment of Fig. 2 will be particularly useful as an athletic running track.

Fig. 3 illustrates another embodiment of this invention where the composite material of this invention is used in a laminated structure useful as a surfacing for a tennis court or the like. In this embodiment, the top surface of the layer 1 of composite is covered with a suitable sealcoat 7 on which is applied a relatively thicker leveling or seam-hiding coat 8 of a suitable resilient material such as polyurethane and the latter then covered with a topcoat 9. Said topcoat 9 can be a polyurethane containing polyvinyl chloride aggregate to provide a non-slip surfacing.

The composite of this invention can also be used in fabricating artificial turf, embodiments of which are shown in Figs. 4 and 5. Referring to Fig. 4, the top of the composite layer 1 is covered with a layer 11 of an energy-absorbing material, preferably a suitable foamed plastic, such as flexible polyurethane foam, polyvinyl chloride foam, nylon foam or polyolefin foam, adhesively bonded to

the composite layer 1 with a suitable adhesive 12. The layer 11 of foamed plastic is then covered with a layer of pile fabric 13 which can be adhesively bonded thereto with a layer 5 14 of a suitable adhesive. The fabric 13 can be of a knitted or tufted type of fabric, the fibers, ribbons, or pile of which simulate that of natural grass. The projecting fibers can be formed from durable, weather resistant 10 plastics, such as nylon, polypropylene, or polyesters. The fibers can be crimped to provide resilience and matting resistance. The fibers can be pigmented to provide any desired color, but green is usually preferred to simulate grass. The pigments used should be color-fast under weather exposure conditions. Ultraviolet light absorbers may also be added to the fibers as needed. In order to form a durable composite structure, the fabric backing 15 to which the fibers are attached preferably should be capable of flexing with the substrate. The backing fabric can be a natural or synthetic fiber such as polyester, (e.g. polyethylene terephthalate) polypropylene or 25 nylon, to which the grass-simulating fibres are secured, for example by looping. The backing can be made with some degree of permeability, for example to permit the adhesive 14 to penetrate the same and ensure anchoring of the pile fabric to the substrate. 30 The backing can be perforated to provide for drainage of water.

The above-described method, in which the composite layer is poured onto the substrate and cured *in situ*, may be preferred for large athletic surfaces, for example football fields. In many applications, however, the artificial turf can be prepared by in-plant fabrication. Such artificial turf can later be applied to the rigid substrate by casting a relatively thin layer of adhesive, preferably a 100% solids urethane reaction mixture. This alternative procedure is particularly advantageous when the surfacing is applied to relative small areas, 45 for example golf greens, tee areas or patios.

Various other materials can be laminated on the novel composite material of this invention, using the composite as a substrate. For example, tiles of polyvinyl chloride or polyvinylchloride-asbestos can be adhesively bonded to the composite and the laminated assembly used for flooring. Also, the composite can be flooded with water and the latter frozen to form an ice-skating surface, the composite used as a substrate for this purpose preferably being water-permeable so as to anchor the layer of ice formed on top of the composite layer, the latter, if desired, being coated on its bottom with a seal coat, 60 for example, made of polyurethane, to prevent drainage of the water therethrough. Though the composite of this invention has been described herein with particular reference to its use as or in surfacing, it can be 65 used for other purposes, such as a crack or

seam filler for construction materials, such as concrete and wood, or it can be shaped in the form of curvilinear articles and used, for example, for drainage or irrigation purposes.

Further objects and advantages of this invention will be illustrated in the following examples.

#### Example 1

A composite of this invention is made based on the following formulation:

TABLE I

	Parts by weight	
Vulcanized rubber particles	400	80
Polypropylene ether glycol (2000 molecular weight)	50	
Polypropylene ether triol (1500 molecular weight)	15	85
Xanthate catalyst	3	
Polymethylene polyphenyl polyisocyanate (Mondur MRS)	32	

The particulate vulcanized rubber of Table I is obtained by abrading or shredding used automobile and truck tire tread and is a blend of vulcanized natural rubber and SBR rubber having the following size distribution.

TABLE II

Fraction, particle size	Wt. %	
Retained on screen with 1.3 cm. openings	2.2	95
Retained on screen with 0.6 cm. openings	3.8	
Retained on U.S. Sieve No. 4	1.6	100
Retained on U.S. Sieve No. 8	10.8	
Retained on U.S. Sieve No. 12	20.8	
Retained on U.S. Sieve No. 20	41.8	
Retained on U.S. Sieve No. 30	9.3	
Through U.S. Sieve 30	9.7	

The xanthate catalyst of Table I is prepared by adding 44 parts by weight of particulate sodium metal to 1000 parts by weight of dipropylene glycol, stirring and heating the mixture to melt the sodium while removing the evolved hydrogen gas. The resulting dipropylene glycol solution of the sodium salt of dipropylene glycol is cooled to 20°C. and 145 parts of carbon disulfide is added thereto to produce a dipropylene glycol solution of the sodium salt of mono-xanthate of dipropylene glycol,  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2(\text{CH}_2)\text{OCS}_2^-\text{Na}^+$ . 115

In preparing the composite, following the formulation of Table I, the glycol, triol, catalyst, and polyisocyanate are mixed in a suitable container to provide a homogeneous solution, the NCO/OH equivalent ratio of the solution being about 2/1. The vulcanized rubber particles are added to this solution and the blend mixed until all of the particles are uniformly wetted or coated with the solu- 125

tion. The mass of coated particles is then poured into a flat rectangular mold, 30.5 cm.  $\times$  61 cm.  $\times$  20 cm. and 368 kg/m<sup>2</sup> pressure is applied to the top of the mass of coated particles while the coating cures. The resulting cured, permeable composite, having a density of about 0.7 g./cc. and a free void space content of about 40 vol. %, is then sliced to provide 0.6 cm. thick slabs of composite. Samples of the composite are tested for physical properties and these are summarized in Table III.

TABLE III

	Tensile strength (ASTM D-412)	5.2 kg/cm <sup>2</sup>
15	Elongation (ASTM D-421)	32.5%
	Tear strength (ASTM D-624, Die C)	4054 g./cm.
	Compression modulus (ASTM D-575)	
20	at 10% compression	1 kg./cm. <sup>2</sup>
	at 50% compression	24.5 kg./cm. <sup>2</sup>
	Impact resilience (ASTM D-2632)	28
25	Hydrolytic stability*	31 days

\*This property is measured by subjecting the sample to an environment of 100°C. and 95% relative humidity, according to the tests described in *Insulation*, August, 1968, p. 39.

After subjecting sample to 100°C., 95% RH environment, no apparent change in the sample is noted, indicating structural integrity is maintained.

## Example 2

An 0.6 cm. thick layer of the composite as described in Example 1 is bonded to an asphalt substrate with a conventional two-part polyurethane adhesive to provide a supported surfacing such as depicted in Fig. 1, useful as a resilient surfacing or pavement for pedestrian or vehicular traffic or for athletic activities. The polyurethane adhesive used as a room-temperature curable adhesive has the following formulation:

TABLE IV  
Part A

		Parts by weight
50	Polypropylene glycol (2000 molecular weight)	50.33
	Litharge catalyst	0.20
	Pigment millbase (a mixture of green and yellow pigments and carbon black in polypropylene glycol, 2000 molecular weight)	1.90
55	Calcium octoate wetting agent	0.40
	Clay filler	46.00
	Ethyl Cellcsolve hardness modified	0.80
60	Asbestos fiber thickener	0.25
	Phenylmercuric acetate catalyst	0.12

## Part B

Polymethylene polyphenyl polyisocyanate (Mondur MRS) 9.0

## Example 3

An athletic running track is prepared by applying to the top of the supported surfacing prepared as described in Example 2 an 0.4 cm. thick layer of the polyurethane formulation shown in Table IV, using an 0.5 cm. notched trowel to apply the formulation to the top of the composite layer. Before the coating of the polyurethane formulation is allowed to cure at ambient conditions, it is sprinkled with cured polyurethane particles having a size range such that the particles used pass through a screen with 0.5 cm. openings. The resulting laminate construction, similar to that depicted in Fig. 2, is useful as an athletic running track.

## Example 4

A surfacing useful as a tennis playing surface is made by applying, first of all, to the top of the supported surfacing structure described in Example 2, a seal-coat of the polyurethane formulation shown in Table IV (but containing about 3 wt. % asbestos fibers), this seal coat being applied with a flat trowel to the top of the composite layer and in an amount sufficient to provide 482 g./m<sup>2</sup>. After this seal coat is allowed to cure to a tack-free condition at ambient temperature, another polyurethane formulation is applied with a notched trowel on top of the seal coat in an amount sufficient to provide 1078 g./m<sup>2</sup> of a level coat. This level coat is allowed to cure at ambient temperature and is made from the following formulation:

TABLE V  
Part A

		Parts by weight
	Polypropylene glycol (PPG-2025, 2000 molecular weight)	52.40
	Polypropylene glycol (PPG 425, 425 molecular weight)	4.50
	Litharge	0.20
	Calcium octoate	0.60
	Clay	47.00
	Phenyl mercuric acetate	0.10

## Part B

Polymethylene polyphenyl polyisocyanate (Mondur MRS) 10.60

In order to provide a non-slip surface, a 0.01 to 0.02 cm. thick conventional moisture-cured polyurethane resin, containing polyvinyl chloride aggregate, is then applied as a topcoat.



### Example 5

Other surfacing made in accordance with this invention, useful as a tennis playing surface or for other athletic purposes, can be prepared in accordance with Example 4 by omitting the level coat and applying the non-slip surfacing directly onto the seal coat. Alternatively, the seal coat and level coat can both be omitted and the non-slip surfacing applied directly to the top of the composite layer. Further, the level coat can be omitted and the non-slip surfacing can be applied to the seal coat, preferably after first sanding the seal coat to provide a smooth surface. A still further modification can be prepared like that described in Example 4 except that the level coat formulation can include polyvinylchloride aggregate and the non-slip surfacing can be omitted. A still further modification can be made by following Example 4 but instead of using the non-slip surfacing, a conventional moisture-cured polyurethane formulation, containing polyvinyl aggregate, can be used, for example with a thickness of 0.01 cm., such a surfacing having a matte finish, this structure being useful, for example, as an indoor playing field for general athletic purposes.

### Example 6

A surfacing, which can be characterized as an artificial turf useful for athletic events such as football, is fabricated by applying a layer of adhesive, having the formulation set forth in Table II, to the exposed or top surface of the supported composite described in Example 2. Before the coating of the adhesive cures, there is applied to it a layer of preformed conventional flexible polyurethane foam, having a high energy absorbing capacity and a density, for example of 160 kg./m<sup>3</sup>. Then another layer of said adhesive is applied to the exposed top of the polyurethane foam and before it cures a pile fabric is placed on it and pressed into place so that the adhesive wets the backing of the pile fabric and a portion of the adhesive penetrates the backing into contact with the pile fibers, thus providing a secure, tenacious bond upon completion of the curing of the adhesive. The pile fabric is a cut, crimped nylon pile, 1.3 cm. in height, placed onto a knitted polyester backing having a total weight of about 1.2 kg/m<sup>2</sup>. The individual nylon fibers are 5 cm. long, circular in cross-section, heat-set crimped with about 8 crimps/cm. so that their length after crimping is about 2.5 cm, the fiber being weather resistant and about 60 denier. The backing is made from 440 denier polyethylene terephthalate yarn which is circularly knitted to include pile fiber in the stitches. The nylon fibers are looped around the backing yarn with each end forming part of the pile. The pile fabric is lightly coated on the back side with an acrylic latex

to improve the dimensional stability and handling of the fabric. The coating is light enough just to coat the yarn of the backing without closing off the spaces between the yarn.

The resulting surfacing or artificial turf is like that depicted in Fig. 4. As a modification thereof, the polyurethane foam layer can be omitted and the pile fabric directly adhesively bonded with said polyurethane adhesive to the exposed top surface of the composite, to provide an artificial turf like that depicted in Fig. 5.

The words "Mondur", "Isonate", "Cello-solve", "Papi", and "Carbitol", as used herein are registered Trade Marks.

### WHAT WE CLAIM IS:—

1. An elastomeric, water permeable composite comprising sulphur-vulcanized rubber particles partially or wholly coated and bonded with a crosslinked, non-cellular, binder having a plurality of isocyanurate and urethane linkages and derived from an essentially solvent-free, polyisocyanate - polyoxyalkylene polyol reaction mixture having low volatility and an NCO/OH equivalent ratio greater than unity.

2. A composite according to claim 1 wherein the rubber particles comprise 50 to 95% by weight, the binder comprises 5 to 50% by weight and wherein the void volume of the composite is in the range 15 to 75%.

3. A composite according to claim 1 or claim 2 wherein the rubber particles comprise comminuted scrap obtained from road vehicle tyres.

4. A shaped article comprising a composite according to any preceding claim.

5. A surfacing comprising a layer of a composite according to any of claims 1 to 3.

6. A surfacing according to claim 5 further comprising one or more lamina of polymeric material overlying the layer.

7. A surfacing according to claim 6 wherein the uppermost lamina has non-slip characteristics.

8. A surfacing according to claim 7 wherein the uppermost lamina has rubbery aggregate embedded therein to provide traction.

9. A surfacing according to claim 5 including a layer of pile fabric overlaying the composite.

10. A surfacing according to claim 9 wherein a layer of energy-absorbing material is interposed between the layer of composite and the layer of pile fabric.

11. A surfacing according to claim 10 wherein the energy absorbing material comprises foamed plastic.

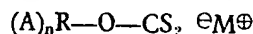
12. A method of making a composite according to claim 1 comprising at least partially coating sulphur-vulcanized rubber particles with a reaction mixture of a cross-linked, non-cellular binder having a plurality



of isocyanurate and urethane linkages and being derived from an essentially solvent-free, polyisocyanate-polyoxyalkylene polyol reaction mixture having low volatility and an NCO/OH equivalent ratio greater than unity; and a trimerizing catalyst, and curing the binder to bind the particles in a coherent mass.

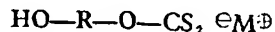
13. A method according to claim 12 wherein the trimerizing catalyst is a xanthate salt.

14. A method according to claim 13 wherein the xanthate salt has the formula



where A is hydroxyl or hydrogen, R is a polyvalent saturated straight or branched chain aliphatic group which can have one or more ether oxygen atoms in said chain, with the proviso that when A is hydrogen said R has one or more of said ether oxygen atoms, n is an integer equal to x-1, where x is the valence of R, and  $M^{\oplus}$  is a cation of an alkali metal or quaternary ammonium.

15. A method according to claim 13 wherein said xanthate salt has the formula



where R is alkyleneoxyalkylene or poly(alkyleneoxyalkylene) and  $M^{\oplus}$  is an alkali metal cation.

16. A method according to any of claims 12 to 15 wherein the polyisocyanate is polymethylene polyphenyl polyisocyanate, the catalyst is mono-sodium dipropylene glycol xanthate and the polyoxyalkylene polyol is polypropylene ether polyol.

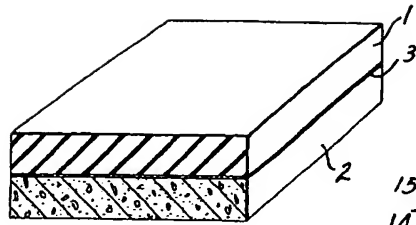
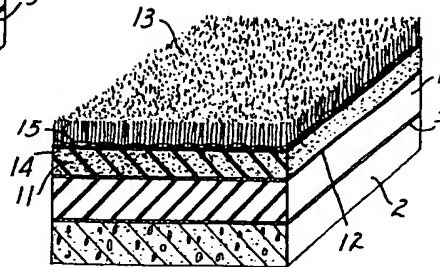
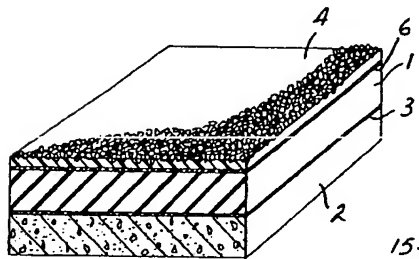
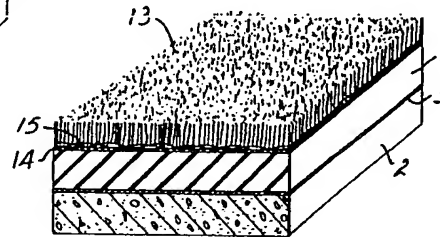
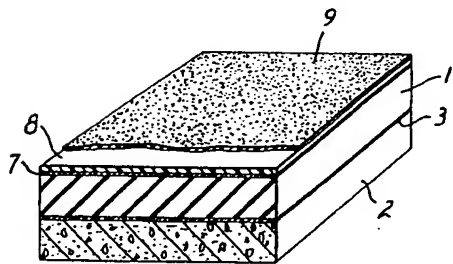
17. A composite substantially as herein described with reference to the Examples.

18. A surfacing comprising a composite according to claim 1 substantially as herein described.

19. A method of making a composite according to claim 1 substantially as herein described.

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**FIG. 1****FIG. 4****FIG. 2****FIG. 5****FIG. 3**